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16. ABSTRACT

This paper describes the chlorination of humic substances in the presence of ammonia and bromide and the resultant formation of trihalomethanes (THMs). Both natural and synthetic waters were studied to isolate the singular and composite effects of ammonia and bromide on the THM formation reaction. Breakpoint chlorination, as well as kinetic experiments, was run for each water. For each breakpoint experiment, measured chlorine demands were compared against theoretical estimates of chlorine utilization on the basis of an assumed set of reactions involving chlorine reacting with ammonia, bromide, and humic substances. The presence of ammonia was found to significantly reduce but not eliminate THM formation at applied chlorine concentrations of less than the breakpoint concentration. Above the breakpoint concentration, THM formation markedly increased in response to the presence of a free chlorine residual. The presence of bromide was found to increase THM yield in the presence or absence of ammonia.

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Chlorine Utilization during Trihalomethane Formation in the Presence of Ammonia and Bromide

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■ This paper describes the chlorination of humic substances in the presence of ammonia and bromide and the resultant formation of trihalomethanes (THMs). Both natural and synthetic waters were studied to isolate the singular and composite effects of ammonia and bromide on the THM formation reaction. Breakpoint chlorination, as well as kinetic experiments, was run for each water. For each breakpoint experiment, measured chlorine demands were compared against theoretical estimates of chlorine utilization on the basis of an assumed set of reactions involving chlorine reacting with ammonia, bromide, and humic substances. The presence of ammonia was found to significantly reduce but not eliminate THM formation at applied chlorine concentrations of less than the breakpoint concentration. Above the breakpoint concentration, THM formation markedly increased in response to the presence of a free chlorine residual. The presence of bromide was found to increase THM yield in the presence or absence of ammonia.

Introduction

Trihalomethanes (THMs) are formed during the chlorination of waters containing precursor compounds, most commonly humic substances (*1*, *2*). Chloroform ($CHCl_3$) is normally the predominant THM species; however, in waters containing bromide ion, brominated haloforms can occur following the oxidation of bromide to hypobromous acid (HOBr) by hypochlorous acid (HOCl) (*3*). Various factors can influence THM formation and speciation including precursor source and concentration, chlorine dose, pH, temperature, and bromide concentration as well as other compounds which react with chlorine such as ammonia (*4–10*).

This paper describes a study of the formation of THMs during the chlorination of a highly colored groundwater from the Biscayne Aquifer in southern Florida. The authors have previously reported on the extent of THM formation following chlorination of this water (*11*). Unusual characteristics of this water are its relatively low, but significant, NH_3–N content and moderate levels of bromide ion (possibly due to saltwater intrusion or dissolution of the coral reef bedrock). In addition to studying this groundwater, several controlled experiments were run with a synthetic water spiked with humic acid, ammonia, and bromide.

The reactions of ammonia and bromide with chlorine are important from a THM control perspective. Ammonia, occurring either naturally or added intentionally to provide chloramine disinfection, exerts a free chlorine demand and reduces ultimate THM levels since chloramines do not react to form THMs (*12*). Bromide is important because it influences THM yield as well as the relative proportions of chloroform and brominated haloforms (*4*, *6*). This latter factor can influence subsequent THM removal technologies since chloroform is more volatile than bromoform during air stripping while bromoform is more effectively adsorbed by activated carbon than chloroform (*13*).

Experimental Methods and Procedures

The first phase of this research was conducted at the Drinking Water Research Center, Florida International University, with a specific sample of water taken from a well associated with the Biscayne Aquifer, hereafter referred to as sample A. THM formation potential (THMFP) experiments were conducted in headspace-free serum vials sealed with Teflon septa and containing aliquots of the groundwater buffered at the ambient pH (7.0) and stored at room temperature (23 °C). Resultant THM species were determined by gas chromatography using the purge-and-trap technique.

The second phase of the research was accomplished at the University of Arizona employing a second sample of the Biscayne Aquifer water, hereafter designated as sample B, taken from the same well approximately 15 months later. The THMFP experiments were similar to those described for sample A with the following exceptions: a reaction temperature of 20 °C was employed; samples were buffered at a slightly higher ambient pH (7.3); THM measurements were made with the liquid/liquid extraction technique and gas chromatography (*14*).

Finally, a series of experiments focusing on synthetic waters were run to develop a better understanding of the behavior of chlorine in the presence of humic substances, ammonia, and bromide. These waters were synthesized by adding to distilled water various combinations of a commercially available, soil-derived humic acid (Aldrich Chemical Co., Milwaukee, WI), NH_4Cl as a source of NH_3–N, and NaBr as a source of bromide ion. The THMFP experiments were identical with those run for sample B of the Biscayne Aquifer except that a pH of 7.0 was utilized (provided by a phosphate buffer).

The various waters were characterized according to precursor-related parameters including nonvolatile total organic carbon (NVTOC) (Dohrmann DC-80 TOC analyzer), UV absorbance (Perkin-Elmer UV–visible spectrophotometer, 1-cm cell), and color, as well as pH, ammonia nitrogen (*15*), bromide (Dionex Model 10 ion chromatograph), total iron and total manganese (Perkin-Elmer atomic absorption spectrophotometer, Model 360).

Results and Discussion

Characterization of Waters. Two different samples of the Biscayne Aquifer were obtained from a well located near the John E. Preston Water Treatment Plant within the Miami–Dade Water and Sewer Authority. The time span between samples was 15 months. Important characteristics of samples A and B are summarized in Table I. On the basis of NVTOC and UV absorbance measurements, it appears that the humic substances content of this water was similar in both samples, while ammonia and bromide varied to a significant degree. Thurman et al. (*16*) studied important characteristics of humic substances isolated from groundwater taken from another location within the Biscayne Aquifer and found that humic substances accounted for approximately two-thirds of the

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Table I. Characteristics of Biscayne Aquifer Samples and Synthetic Waters

parameter	Biscayne Aquifer sample A (7/14/81)	Biscayne Aquifer sample B (10/26/82)	synthetic waters
NVTOC, mg/L	6.0	6.5	3.33
UV absorbance (254 nm and pH 7)	0.269	0.251	0.320
color, color units		38	125
pH	7.0	7.31	7.0
NH_3–N, mg/L	2.0	0.8	0.0 or 1.0
Br^-, mg/L	0.25	0.16	0.0 or 1.0
total Fe, mg/L		0.6	0.0
total Mn, mg/L		0.0	0.0

NVTOC and the molecular weights of isolated humic substances ranged from 500 to 2000.

The synthetic waters, hereafter referred to as S-1 through S-4, are also characterized in Table I. These waters were prepared to study the effects of ammonia and bromide. Water S-1 contained neither ammonia nor bromide, S-2 contained ammonia alone, S-3 contained bromide alone, and S-4 contained both ammonia and bromide. The ammonia and bromide levels shown in Table I for the synthetic waters represent added amounts. However, analysis of water S-1 indicated no bromide present at the detection limit while the NH_3–N level was determined to be less than 0.1 mg/L. Precursor-related parameters and pH were held constant for all synthetic waters in order to isolate the effects of ammonia and bromide.

Breakpoint Chlorination Experiments. Results derived from the chlorination of samples A and B of the Biscayne Aquifer are presented in Figures 1 and 2. Corresponding results for synthetic waters are shown in Figures 3 and 4.

Figure 1 presents the experimentally determined breakpoint chlorination curves for samples A and B based on reaction times of 2 and 1 h, respectively, as well as the corresponding THM formation as a function of applied chlorine. The theoretical breakpoint chlorination concentrations for samples A and B are 16.0 and 6.4 mg/L, respectively, on the basis of a Cl_2 to NH_3–N weight ratio of 8.0 (*17*). The theoretically expected shape of a breakpoint chlorination curve involves three distinct phases: a first phase whereby chlorine residual increases with applied chlorine up to an approximate Cl_2 to NH_3–N molar ratio of 1:1 (corresponding to chloramine formation), a second phase in which chlorine residual decreases with applied chlorine in the molar ratio range of about 1:1 to 1.6:1 (corresponding to breakpoint oxidation to N_2 and possibly some NO_3^-), and a third phase in which chlorine residual increases with applied chlorine at molar ratios of above about 1.6:1 (corresponding to the appearance of a free chlorine residual). Note that Cl_2 to NH_3–N molar ratios of 1:1 and 1.6:1 correspond to weight ratios of approximately 5:1 and 8:1, respectively.

Figure 1 also presents the formation of THMs as a function of applied chlorine concentration for reaction conditions identical with those of the breakpoint chlorination experiments. These results indicate that THMs form at chlorine concentrations less than that needed to reach the breakpoint. At each chlorine concentration tested, the collective sum of the brominated haloform concentrations constituted a significant portion of the total THMs for sample A (2-h reaction time). This effect was particularly pronounced at the highest applied chlorine concentration where the sum of brominated haloforms was higher than the chloroform concentration. For sample B

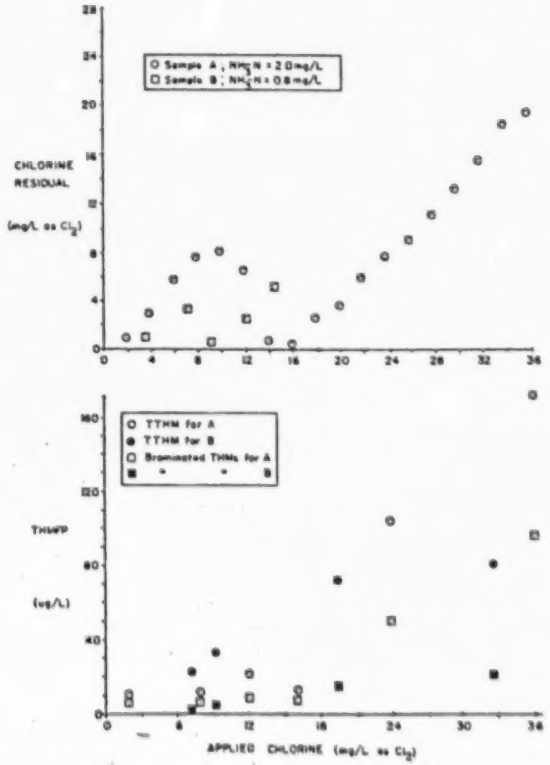

Figure 1. Breakpoint chlorination curves and THM formation as a function of applied chlorine for Biscayne Aquifer samples. Two- and 1-h reaction times for samples A and B containing 2.0 and 0.8 mg/L NH_3–N, respectively.

(1-h reaction time), brominated haloform constituted a much lower percentage of the total THMs, a response influenced largely by the lower bromide content of sample B.

The results given in Figure 2 describe the THMFP of samples A and B, respectively, as a function of reaction time at each of four different chlorine concentrations including the experimentally determined breakpoint concentration, one subbreakpoint concentration, and two superbreakpoint concentrations (see Figure 1). At concentrations above the breakpoint concentration, significant levels of THMs were observed, while THM formation was evident but strongly suppressed at concentrations of less than or equal to the breakpoint concentration.

Applied chlorine vs. residual chlorine curves for the four synthetic waters are presented in Figure 3 on the basis of a reaction time of 1 h. Also presented in Figure 3 is THM formation as a function of applied chlorine concentration for reaction conditions identical with those of the breakpoint chlorination experiments. The curves shown in the top graphic in Figure 3 pertain to synthetic waters *not* containing ammonia (S-1 and S-3). The measured chlorine residual was less than each applied chlorine concentration, indicating that there was a measurable chlorine consumption as a result of reactions involving chlorine and humic substances. The results presented in the middle graphic of Figure 3 are derived from synthetic waters containing ammonia (S-2 and S-4). These experimentally derived curves resemble the characteristic shape of a theoretical breakpoint chlorination curve, although the experimental curves are shifted to the right of the theoretically expected curve. The theoretical breakpoint chlorination concentration is 8.0 mg/L on the basis of a Cl_2 to NH_3–N weight ratio of 8.0. This shift in behavior

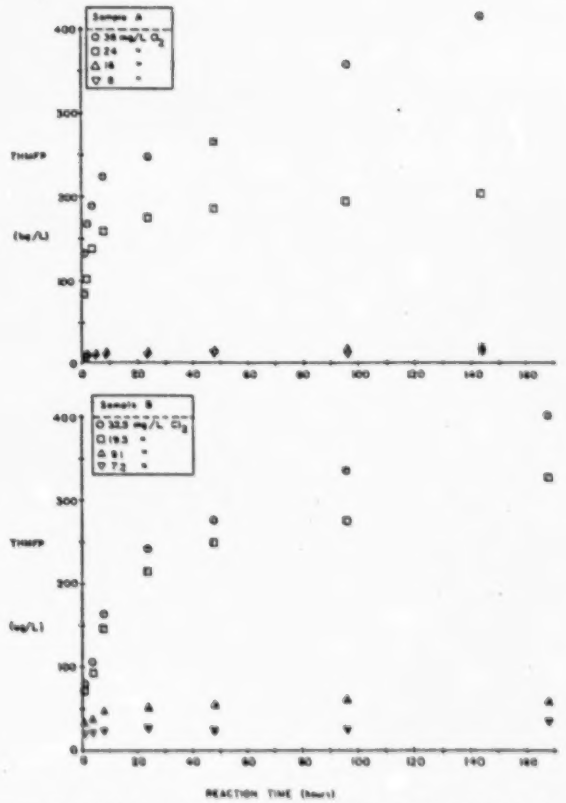

Figure 2. THM formation as a function of time for samples A and B of Biscayne Aquifer.

reflects the chlorine demand associated with the humic substances.

The bottom graphic of Figure 3 portrays THM formation as a function of applied chlorine concentration for the four synthetic waters, based on a reaction time of 1 h. The formation curves for waters containing no ammonia (S-1 and S-3) indicate that the THMFP initially increases sharply as a function of applied chlorine concentration and ultimately approaches a "plateau" at a chlorine concentration of about 12 mg/L or greater. In contrast, formation curves associated with waters containing ammonia (S-2 and S-4) are characterized by apparent S-shaped curves. At lower chlorine concentrations, it appears that the reactions with ammonia predominate, thereby minimizing THM formation. At higher chlorine concentrations, THM formation begins to increase significantly as a function of applied concentration until a plateau is reached, where increasing chlorine concentrations have much less effect on THM formation.

The formation of THMs as a function of time for each of the synthetic waters is shown in Figure 4. These results are based on an applied chlorine concentration of 10 mg/L. It is apparent that the presence of ammonia suppresses but does not eliminate THM production. Moreover, the presence of bromide increases THM formation (in terms of $\mu g/L$) both in the presence and in the absence of ammonia. It should be noted that bromide also enhanced THM formation on a molar yield basis.

Analysis of Chlorine Utilization. On the basis of the results presented in Figures 1–4, it is apparent that the chlorination of humic substances in the presence of ammonia and bromide constitutes a complex chemical system involving competing reactions characterized by unique kinetics and equilibria. The more important reactions

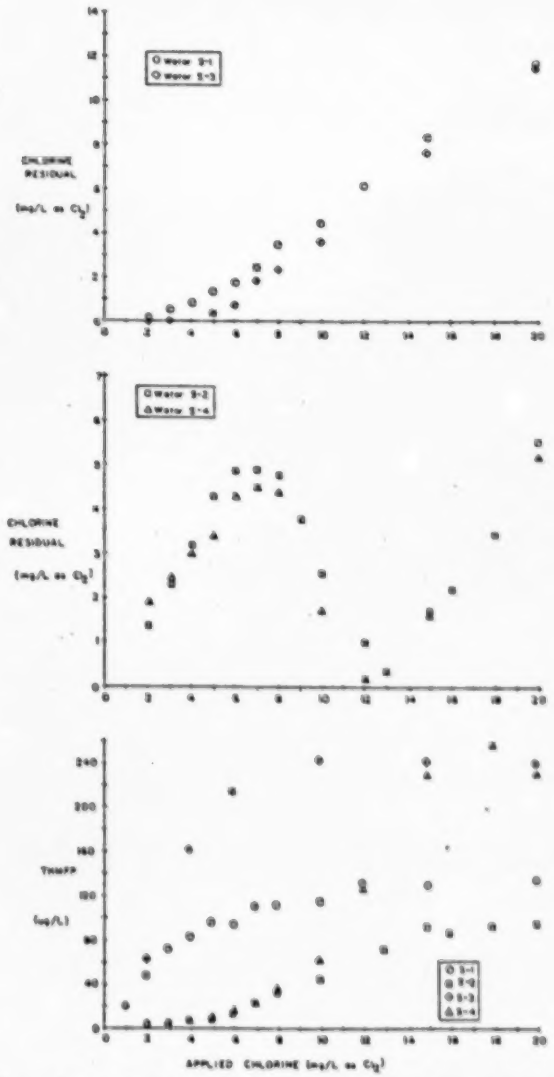

Figure 3. Breakpoint chlorination curves and THM formation as a function of applied chlorine for synthetic waters. One-hour reaction time. Waters S-1 and S-3 contain no ammonia while waters S-2 and S-4 contain 1 mg/L NH_3–N; waters S-1 and S-2 contain no bromide while waters S-3 and S-4 contain 1 mg/L bromide.

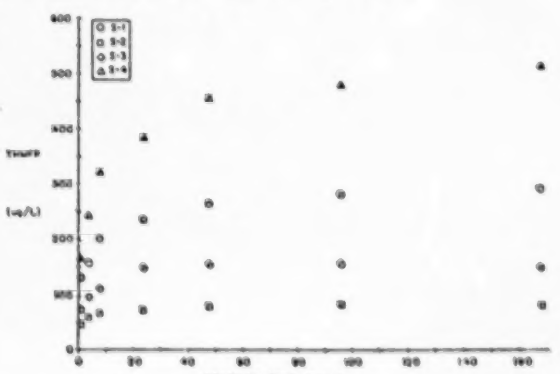

Figure 4. THM formation as a function of time for synthetic waters. Based on applied chlorine concentration of 10 mg/L.

associated with this system are detailed in the literature (*3*, *17–31*). Important reactions include those involving

chlorine (hypochlorous acid) as well as bromine (hypobromous acid) which is produced by chlorine oxidation of bromide. These include chloramine formation, breakpoint oxidation, bromide oxidation. bromamine formation, chlorinated organo N compound formation, brominated organo N compound formation, bromochloramine formation, decomposition of chloramines and bromamines, oxidation of humic substances, and trihalomethane formation.

The relative predominance of the associated reactions is influenced by many factors including reaction rate constants, reactant concentrations, and pH conditions. Considering the experimental conditions employed, the most important reactions involving chlorine consumption are assumed to be monochloramine formation, breakpoint oxidation, oxidation of bromide, humic oxidation, and trihalomethane formation. While the stoichiometry and kinetics are well-defined for certain of these reactions, they are not well-defined for reactions involving humic oxidation and THM formation.

By use of the stoichiometric relationships associated with the above reactions, as detailed in the literature (*3, 17–31*), it is possible to estimate a theoretical chlorine utilization for a given set of experimental conditions. This procedure permits a comparison of theoretical vs. measured chlorine utilization. In order to account for chlorine utilization in the presence of humic substances, ammonia, and bromide, the following assumptions are made: (1) monochloramine formation predominates over other *N*-chloro reactions during the initial first phase (i.e., upslope) of the breakpoint curve corresponding to a Cl_2 to NH_3–N molar ratio of approximately 1:1, (2) the breakpoint reaction will be the principal *N*-chloro reaction occurring during the second phase (i.e., downslope) of the breakpoint curve (i.e., the breakpoint condition), (3) some degree of bromide oxidation to hypobromous acid will occur in parallel with other reactions, and (4) humic oxidation and THM formation will occur, to varying extents, at all chlorine doses.

In order to assist in this analysis to account for chlorine utilization, an examination of the findings of other researchers (*12, 32*) as well as the results of previous studies conducted in the authors' laboratories was undertaken to establish chlorine utilization during humic oxidation and corresponding THM formation. On the basis of data derived from six natural waters and four synthetic waters, it was determined that the ratio of TTHM formed to chlorine utilized ranges from 26 to 51 μg/mg with a mean of 35 and a standard deviation of 8.1. These results were derived from experiments involving varying reaction times up to 168 h and waters with varying amounts of bromide.

As indicated earlier, total chlorine residuals were measured by amperometric titration. It is important to recognize that chlorine-related species other than free chlorine such as chloramines as well as certain bromine-related species such as hypobromous acid and bromamines appear as part of the measured chlorine residual. Thus, although oxidation of Br^- to HOBr by HOCl represents a theoretical chlorine demand, this does not appear as part of the measured chlorine demand.

An analysis of measured vs. theoretical chlorine utilization is presented in Table II for each of three applied chlorine conditions: the experimentally determined breakpoint concentration, selected subbreakpoint concentrations, and selected superbreakpoint concentrations. For each of these conditions, the measured chlorine utilization is compared against the theoretical chlorine utilization for each water.

Values of measured chlorine utilization were estimated by subtracting the measured total chlorine residual from the applied chlorine concentration. In effect, the measured utilization represents a measured chlorine demand. These estimates were based on a reaction time of 2 h for sample A and a reaction time of 1 h for sample B as well as waters S-1 through S-4.

Estimates of theoretical chlorine utilization were made for each applied chlorine condition and each water by considering pertinent reactions associated with each phase of the breakpoint chlorination curve. These estimates were based on the stoichiometry of the breakpoint reaction as well as approximations of chlorine consumption during humic oxidation and THM formation. The average value of 35 μg of THMs formed per mg of Cl_2 consumed was used to approximate the utilization of chlorine during the complex set of reactions involving humic oxidation and THM formation. Chlorine consumed by bromide oxidation was not considered as part of the theoretical utilization because the resultant HOBr would appear as part of the measured chlorine residual. In a likewise manner, chloramine formation was not included in this analysis since any chloramines formed were measured as part of the total chlorine residual.

The first results summarized in Table II are associated with the observed breakpoint chlorine concentration. Note that applied chlorine concentrations for synthetic waters not containing ammonia were chosen to approximately coincide with breakpoint concentrations observed for synthetic waters containing ammonia. The theoretical chlorine utilization for each water was estimated from the stoichiometry of the breakpoint reaction as well as the chlorine utilization associated with humic oxidation and THM formation. The data indicate that the theoretical chlorine utilization in all cases was less than the observed chlorine demand. With the exception of sample A, the differences between measured vs. theoretical chlorine utilization were about 1–2 mg/L.

An analysis of measured vs. theoretical chlorine utilization at selected subbreakpoint concentrations also appears in Table II. The concentrations were chosen from the first phase (i.e., upslope) of the breakpoint curves and, thus, are coincident with chloramine formation. As before, the experimentally determined chlorine utilization or demand was determined by the difference between applied concentration and measured residual. Calculations of theoretical chlorine utilization were based on chlorine requirements for humic oxidation and THM formation. These calculations do not consider chloramine formation since chloramines appear as part of the measured chlorine residual. With the exception of sample B, discrepancies between measured vs. theoretical chlorine utilization were less than 1 mg/L.

Finally, Table II summarizes an analysis of measured vs. theoretical chlorine utilization at selected superbreakpoint concentrations. These concentrations were selected to coincide with applied chlorine concentrations significantly beyond the breakpoint condition where virtually all of the chlorine residual would exist as free chlorine. Applied concentrations for synthetic waters not containing ammonia were chosen to coincide with concentrations selected for synthetic waters containing ammonia. With the exception of sample A, the theoretical chlorine utilization is significantly less than the experimentally observed chlorine demand. These differences may be partly attributed to a phenomenon whereby, at excessively high chlorine doses, more chlorine is utilized in the oxidative destruction of humic acid molecules to create byproducts

Table II. Measured vs. Theoretical Chlorine Utilization

Breakpoint Concentration

	Biscayne Aquifer		synthetic waters			
	A	B	S-1	S-2	S-3	S-4
measured chlorine utilization, mg/L as Cl_2						
applied concentration	16.0	9.10	12.0[a]	13.0	12.00[a]	12.0
measured residual	0.40	0.60	6.05	0.45	5.25	0.2
measured utilization	15.6	8.50	5.95	12.55	6.75	11.8
theoretical chlorine utilization, mg/L as Cl_2						
breakpoint concentration	15.2	6.09	0	7.60	0	7.60
humic oxidation and THM formation	0.31	0.94	4.67	2.62	5.55	2.87
	15.51	7.03	4.67	10.22	5.55	10.47

Selected Subbreakpoint Concentrations

	Biscayne Aquifer		synthetic waters			
	A	B	S-1	S-2	S-3	S-4
measured chlorine utilization, mg/L as Cl_2						
applied concentration	8.00	3.50	4.00	4.00	4.00	4.00
measured residual	7.42	1.30	0.80	3.20	0.30	3.00
measured utilization	0.58	2.20	3.20	0.80	3.70	1.00
theoretical chlorine utilization, mg/L as Cl_2						
humic oxidation and THM formation	0.33	0.66	2.98	0.21	3.72	0.14
	0.33	0.66	2.98	0.21	3.72	0.14

Selected Superbreakpoint Concentrations

	Biscayne Aquifer		synthetic waters			
	A	B	S-1	S-2	S-3	S-4
measured chlorine utilization, mg/L as Cl_2						
applied concentration	24.0	19.5	20.0	20.0	20.0	20.0
measured residual	7.42	9.0[b]	11.6	5.25	11.4	5.20
measured utilization	16.58	10.5	8.4	14.75	8.6	14.80
theoretical chlorine utilization, mg/L as Cl_2						
breakpoint concentration	15.2	6.09	0	7.60	0	7.60
humic oxidation and THM formation	3.09	2.06	4.79	3.46	5.55	5.29
	18.29	8.15	4.79	11.06	5.55	12.89

[a] Applied concentrations for synthetic waters not containing ammonia were chosen to approximately coincide with breakpoint concentrations observed for synthetic waters containing ammonia. [b] Estimated value derived from extrapolation of observed breakpoint curve.

less susceptible to THM formation.

Overall, the results appearing in Table II indicate that it is possible, from theoretical considerations, to account for most of the observed chlorine utilization during the chlorination of waters containing humic substances, ammonia, and bromide. Discrepancies between the measured and theoretical utilization of chlorine can be attributed to the following factors: (1) other chlorine-demanding reactions not considered in the analysis such as the oxidation of inorganic reducing agents (Fe^{2+} and Mn^{2+}) and the oxidative destruction of humic substances to produce both chlorinated and nonchlorinated organic byproducts; (2) the occurrence of breakpoint reactions involving end products other than mostly N_2 and possibly some NO_3^-; and (3) the lack of precision in estimating the quantity of THMs formed per unit mass of chlorine utilized. This latter quantity varies with many parameters such as pH, temperature, bromide concentration, reaction time, and nature of the precursor material. Qualls and Johnson (*31*) have demonstrated that the chlorine demand of fulvic acid occurs in two types of reactions: an initial rapid reaction and a slower long-term reaction.

Conclusions

The presence of ammonia substantially reduces but does not eliminate THM production during the chlorination of waters containing humic substances. This behavior has important implications for water utilities that (1) use a raw water source containing low but significant levels of ammonia such as the Biscayne Aquifer or (2) are considering chloramine disinfection as a THM control strategy.

The presence of bromide ion in waters containing humic substances leads to increased THM formation, both in the presence and in the absence of ammonia. In waters containing ammonia, bromide, and humic substances, brominated haloforms can form upon chlorination; however, brominated species comprise a larger portion of the total THMs at higher chlorine doses within the free chlorine region of the breakpoint curve than at lower doses in the subbreakpoint region.

Although the THM formation reaction is slow and may not be complete even after 1 week of reaction time, the initial rate of formation is competitive with the relatively rapid reactions of bromide oxidation and chloramine formation. After free chlorine is converted to chloramines, THM production should theoretically cease; however, THMs will form in parallel with chloramine formation.

Registry No. NH_3, 7664-41-7; Br^-, 24959-67-9.

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